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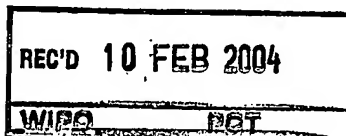
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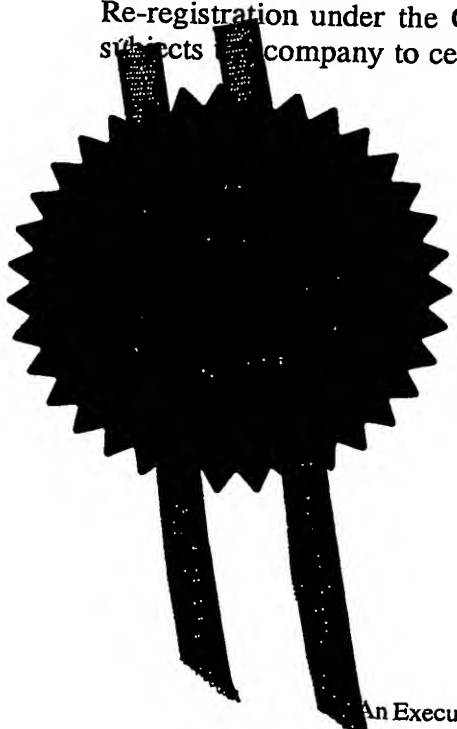
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*P. Mahoney*

Dated

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28DEC02 E773707-1 D00192  
P01/7700 0.00-0230156.2

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Cardiff Road  
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1. Your reference

N87219 PEJ

2. Patent application number

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0230156.2

24 DEC 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Oxonica Limited  
7 Begbroke Science & Business Park  
Sandy Lane, Yarnton, Kidlington  
Oxford OX15 1PF

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

British body corporate

08/47 845001

4. Title of the invention

SUNSCREENS

5. Name of your agent (if you have one)

J.A. KEMP & CO.

"Address for service" in the United Kingdom to which all correspondence should be sent (Including the postcode)

14 South Square  
Gray's Inn  
London  
WC1R 5JJ

Patents ADP number (if you know it)

26001

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Number of earlier application

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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11. I/We request the grant of a patent on the basis of this application.

Signature

*J.A. Kemp & Co.*  
J.A. KEMP & CO.

Date 24 December 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

PGA Ellis-Jones  
020 7405 3292

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## SUNSCREENS

DUPLICATE

The present invention relates to UV screening compositions suitable for cosmetic use.

5 The effects associated with exposure to sunlight are well known. Thus exposure of the skin to UVA and UVB light may result in, for example, sunburn, premature ageing and skin cancer.

Commercial sunscreens generally contain components which are able to reflect and/or absorb UV light. These components include, for example, inorganic  
10 oxides such as zinc oxide and titanium dioxide as well as organic sunscreen agents.

The general public are generally more concerned by the obvious effects of sunlight, namely sunburn which causes reddening of the skin than they are with other effects of sunlight which are less self evident. As a consequence of this commercial  
15 sunscreen compositions are rated by a Sun Protection Factor (SPF). This is a measure of the time taken for skin to redden under a layer of the composition as compared with untreated skin. Thus an SPF of 20 indicates that skin will take 20 times longer to redden under a layer of the composition applied at 2mg per cm<sup>2</sup> compared with untreated skin. This reddening effect is caused principally by UVB  
20 light. There is no recognised corresponding factor for the effects of UVA light even though the latter may be more damaging in the long term.

Most organic sunscreen agents absorb light over only a part of the UVA-UVB spectrum with the result that if one is to obtain a screening effect covering the whole UVA-UVB spectrum it is generally necessary to use a combination of different organic sunscreen agents. Some organic sunscreen agents and other components of  
25 sunscreen compositions are stable to UV light but others are photosensitive and/or may after being excited by UV light degrade another ingredient of the composition.

Titanium dioxide and zinc oxide are generally formulated as "micronised" or "ultrafine" (20-50 nm) particles (so-called microreflectors) because particles whose size is less than 10% of the wavelength of the incident light scatter light according to  
30 Rayleigh's Law, whereby the intensity of scattered light is inversely proportional to the fourth power of the wavelength. Consequently, they scatter UVB light (with a wavelength of from 290 to 320 nm) and UVA light (with a wavelength of from 320 to 400 nm) more than the longer, visible wavelengths, preventing sunburn whilst

remaining invisible on the skin.

However, titanium dioxide and zinc oxide also absorb UV light efficiently, leading via the initial formation of electron hole pairs to the formation of superoxide and hydroxyl radicals and which may in turn initiate damage to other components of the composition. The crystalline forms of  $\text{TiO}_2$ , anatase and rutile, are  
5 semiconductors with band gap energies of about 3.23 and 3.06 eV respectively, corresponding to light of about 385 nm and 400 nm (1 eV corresponds to  $8066 \text{ cm}^{-1}$ ). Indeed there is evidence to suggest that  $\text{TiO}_2$  can enhance the degradation of organic sunscreen agents, including UVA organic sunscreens, for example oxybenzone.  
10 Attempts have been made to reduce the adverse effects of  $\text{TiO}_2$  and  $\text{ZnO}$  by coating but coatings are not invariably effective.

The reason why a sunscreen agent does not have a substantially perpetual effect (i.e. an SPF factor which is substantially infinite) is because the organic sunscreen agents are degraded by light and/or are adversely affected by other  
15 components of the sunscreen composition once the latter are subjected to UV light.

It has now surprisingly been found, according to the present invention, that the degradation of organic sunscreen agents, and other components which are susceptible to degradation, can be retarded if the compositions also have present zinc oxide or titanium dioxide which has been doped with a second element. In other  
20 words by using these doped materials rather than ordinary titanium dioxide or zinc oxide it is, for example, possible either to provide a composition which gives better protection against UV light for the same quantity of organic sunscreen agent or a composition having the same screening effect against UV light but containing a smaller quantity of organic sunscreen agent.

Accordingly the present invention provides a cosmetic UV suncreening composition which comprises an amount of one or more organic components which are photosensitive and/or which are degraded by another ingredient of the composition, optionally together with an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has not been doped with a second element and an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has  
30 been doped with a second element, this composition having a rate of loss of UV absorption at least 5% less than that of a composition having the same formulation

except that it does not contain the said  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has been doped with a second element. Thus if the rate of loss of UV absorption over at least a proportion of the UVA and/or UVB spectrum is X then the amount of the organic component(s) which are photosensitive and/or which are degraded by another ingredient of the composition, optionally together with the amount of undoped  $\text{TiO}_2$  and/or  $\text{ZnO}$ , possesses a said rate of loss of Y where Y is greater than X by at least 5%, and the amount of doped  $\text{TiO}_2$  and/or  $\text{ZnO}$  reduces the said rate of loss from Y to X. The present invention also provides the use of a doped  $\text{TiO}_2/\text{ZnO}$  to reduce the concentration of one or more organic UV sunscreen or other photosensitive ingredient or ingredient which is degraded by another ingredient of the composition in a cosmetic UV screening composition as well as to reduce the rate of loss in UV absorption of a sunscreen composition containing one or more organic UV sunscreen agents. The present invention further provides a method of increasing the effectiveness of an organic sunscreensing composition which comprises one or more components which are photosensitive and/or which are degraded by another ingredient of the composition which comprises incorporating into the composition a doped  $\text{TiO}_2/\text{ZnO}$ .

By "cosmetic UV sunscreensing composition" is meant any cosmetic composition having UV sunscreensing activity i.e. it includes compositions whose principal function may not be sunscreensing. It will be appreciated that the doped  $\text{TiO}_2/\text{ZnO}$  may be the only ingredient of the composition having UV sunscreensing activity i.e. the composition need not necessarily contain an organic UV sunscreen agent.

The organic component which is photosensitive or degraded by another ingredient of the composition is generally a UV sunscreen agent. Although all organic sunscreen agents which suffer a loss in UV absorption can be used, the present invention is particularly useful for agents which absorb in the UVA region. However, other organic components will generally be susceptible to free radical attack and in turn this generally will cause degradation of the UV sunscreen agent.

The rate of loss of absorption can be determined by illuminating a sample of the composition with and without the doped  $\text{TiO}_2$  and/or  $\text{ZnO}$  of defined thickness

with UV light of the appropriate wavelength and determining the absorption of UV by the composition over a given period, typically 60 minutes, obtaining a plot over that period for the wavelengths in question and determining the area under the curve from which the rate of loss can be calculated. Clearly the smaller the area under the curve the smaller the loss. For UVA absorption wavelengths from 320 to 400, especially from 340 to 390 nm, are considered.

While any reduction in the loss of UV absorption is an advantage, it is generally desirable that the presence of the doped oxide should reduce the rate of UV absorption by an amount of at least a 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

The dopant for the oxide particles is preferably manganese, which is especially preferred, e.g.  $Mn^{2+}$  but especially  $Mn^{3+}$ , vanadium, for example  $V^{3+}$  or  $V^{5+}$ , chromium and iron but other metals which can be used include nickel, copper, tin, aluminium, lead, silver, zirconium, zinc, cobalt, gallium, niobium, for example  $Nb^{5+}$ , antimony, for example  $Sb^{3+}$ , tantalum, for example  $Ta^{5+}$ , strontium, calcium, magnesium, barium, molybdenum, for example  $Mo^{3+}$ ,  $Mo^{5+}$  or  $Mo^{6+}$  as well as silicon. Manganese is preferably present as  $Mn^{3+}$ , cobalt as  $Co^{2+}$ , tin as  $Sn^{4+}$  as well as  $Mn^{2+}$ . These metals can be incorporated singly or in combination of 2 or 3 or more. Further details of these doped oxides can be found in WO99/60994 as well as WO01/40114.

The average primary particle size of the particles is generally from about 1 to 200 nm, for example about 1 to 150 nm, preferably from about 1 to 100 nm, more preferably from about 1 to 50 nm and most preferably from about 20 to 50 nm. The particle size is preferably chosen to avoid colouration of the final product.

Where particles are substantially spherical then particle size will be taken to represent the diameter. However, the invention also encompasses particles which are non-spherical and in such cases the particle size refers to the largest dimension.

The optimum amount of the second component in the host lattice may be determined by routine experimentation but it is preferably low enough so that the particles are not coloured. Amounts as low as 0.1 mole % or less, for example 0.05 mole %, or as high as 1 mole % or above, for example 5 mole % or 10 mole %, can

generally be used. Typical concentrations are from 0.5 to 2 mole % by weight.

These particles can be obtained by any one of the standard processes for preparing doped oxides and salts. Thus they can be obtained by a baking technique by combining particles of a host lattice ( $\text{TiO}_2/\text{ZnO}$ ) with a second component in the form of a salt such as a chloride or an oxygen-containing anion such as a perchlorate or a nitrate, in solution or suspension, typically in solution in water, and then baking it, typically at a temperature of at least  $300^\circ\text{C}$ . Other routes which may be used to prepare the doped materials include a precipitation process of the type described in J. Mat. Sci. (1997) 36, 6001-6008 where solutions of the dopant salt and of an alkoxide of the host metal (Ti/Zn) are mixed, and the mixed solution is then heated to convert the alkoxide to the oxide. Heating is continued until a precipitate of the doped material is obtained. Further details of preparation can be found in the aforesaid patent specifications.

The rutile form of titania is known to be more photostable than the anatase form and is therefore preferred.

The oxide particles of the present invention may have an inorganic or organic coating. For example, the particles may be coated with oxides of elements such as aluminium, zirconium or silicon. The particles of metal oxide may also be coated with one or more organic materials such as polyols, amines, alkanolamines, polymeric organic silicon compounds, for example,  $\text{RSi}[\{\text{OSi}(\text{Me})_2\}_x\text{OR}^1]_3$  where R is  $\text{C}_1\text{-C}_{10}$  alkyl,  $\text{R}^1$  is methyl or ethyl and x is an integer of from 4 to 12, hydrophilic polymers such as polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants such as, for example, TOPO.

The compositions of the present invention may be, for example, lipsticks, skin anti-ageing compositions in the form of, for example, creams, exfoliating preparations including scrubs, creams and lotions, skin lightening compositions in the form of, for example, face powders and creams, preparations for the hands including creams and lotions, moisturising preparations, compositions for protecting the hair such as conditioners, shampoos and hair lacquers as well as hair masks and gels, skin cleansing compositions including wipes, lotions and gels, eye shadow and blushers, skin toners and serums as well as washing products such as shower gels,



bath products including bubble baths, bath oils, but, preferably, sunscreens. In this connection we should point out that the expression "cosmetic UV suncreening composition", as used herein, includes any composition applied to the skin which may leave a residue on the skin such as some washing products. Compositions of the present invention may be employed as any conventional formulation providing protection from UV light.

Organic sunscreen agents which can be used in the compositions of the present invention include any conventional sunscreen agent which gives protection against UV light while if there is no other photosensitive component the sunscreen agent is photosensitive and/or is degraded by another ingredient of the composition. Suitable sunscreen agents are listed in the IARC Handbook of Cancer Prevention, vol. 5, Sunscreens, published by the International Agency for research on cancer, Lyon, 2001 and include:

- (a) Para-aminobenzoic acids (PABA), (UVB absorbers) esters and derivatives thereof, for example amyldimethyl-; ethyldihydroxypropyl-; ethylhexyl dimethyl-; ethyl-; glyceryl-; and 4-bis-(polyethoxy)- PABA.
- (b) Cinnamates (UVB) especially esters including methyl cinnamate esters and methoxycinnamate esters such as octylmethoxy cinnamate, ethyl methoxycinnamate, especially 2-ethylhexyl para-methoxycinnamate, isoamyl p-methoxy cinnamate, or a mixture thereof with diisopropyl cinnamate, 2-ethoxyethyl -4-methoxycinnamate, DEA-methoxycinnamate (diethanolamine salt of para-methoxy hydroxycinnamate) or  $\alpha,\beta$ -di-(para-methoxycinnamoyl)- $\alpha'$ -(2-ethylhexanoyl)-glycerin, as well as diisopropyl methylcinnamate;
- (c) benzophenones (UVA) such as 2,4-dihydroxy-; 2-hydroxy-4-methoxy-; 2,2'-dihydroxy-4,4'-dimethoxy-; 2,2'-dihydroxy-4-methoxy-; 2,2',4,4'-tetrahydroxy-; and 2-hydroxy-4-methoxy-4'-methyl-benzophenones, benzenesulphonic acid and its sodium salt; sodium 2,2'-dihydroxy-4,4'-dimethoxy-5-sulphobenzophenone and oxybenzone;

- (d) dibenzoylmethanes (UVA) such as butyl methoxydibenzoyl methane, especially 4-tert-butyl-4'methoxydibenzoylmethane;
- (e) 2-phenylbenzimidazole-5 sulfonic acid UVB and phenyldibenzimidazole sulfonic acid and their salts;
- 5 (f) alkyl- $\beta,\beta$ -diphenylacrylates (UVB) for example alkyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylates such as octocrylene;
- (g) triazines (UVB) such as 2,4,6-trianilino-(p-carbo-2-ethyl-hexyl-1-oxy)-1,3,5 triazine as well as octyl triazone e.g. ethylhexyltriazone and diethylhexyl butamido triazone.
- 10 (h) camphor derivatives (generally UVB) such as 4-methylbenzylidene and 3-benzylidene- camphor and terephthalylidene dicamphor sulphonic acid (UVA), benzylidene camphor sulphonic acid, camphor benzalkonium methosulphate and polyacrylamidomethyl benzylidene camphor;
- 15 (i) organic pigment sunscreens agents such as methylene bis-benzotriazole tetramethyl butylphenol;
- (j) silicone based sunscreens agents such as dimethicodiethyl benzal malonate.
- 20 (k) salicylates (UVB) such as dipropylene glycol-, ethylene glycol-, ethylhexyl-, isopropylbenzyl-, methyl-, phenyl-, 3,3,5-trimethyl- and TEA-salicylate (compound of 2-hydroxybenzoic acid and 2,2'2"-nitrilotris (ethanol));
- (l) anthranilates (UVA) such as menthyl anthranilate as well as bisimidazylate (UVA), dialkyl trioleate (UVB), 5-methyl-2-phenylbenzoxazole (UVB) and urocanic acid (UVB).
- 25

Some compounds are effective for both UVA and UVB. These include anisotriazine, methylene bisbenzotriazolyl tetramethylbutyl- phenol and drometrizole trisiloxane (Mexoryl XL).

The organic sunscreen agent(s) are typically present in the compositions at a  
30 concentration from 0.1 to 20%, preferably 1 to 10%, and especially 2 to 5%, by

weight based on the weight of the composition.

In the compositions the metal oxides are preferably present at a concentration of about 0.5 to 20 % by weight, preferably about 1 to 10 % by weight and more preferably about 3 to 8 % by weight, in particular about 4 to 7%, such as 4 to 6% for example about 5%, by weight.

The compositions may be in the form of, for example, lotions, e.g. thickened lotions, gels, vesicular dispersions, creams, milks, powders, solid sticks, and may be optionally packaged as aerosols and provided in the form of foams or sprays.

The compositions may contain any of the ingredients used in such formulations including fatty substances, organic solvents, silicones, thickeners, demulcents, other UVA, UVB or broad-band sunscreen agents, antifoaming agents, moisturizing agents, perfumes, preservatives, surface-active agents, fillers, sequesterants, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, alkalizing or acidifying agents, colorants and metal oxide pigments with a particle size of from 100 nm to 20000 nm such as iron oxides along with conventional (undoped)  $\text{TiO}_2$  and  $\text{ZnO}$ .

It is known that other ingredients of cosmetic compositions, for example some surface-active agents may have the effect of degrading certain sunscreen agents in the presence of UV light. Also  $\text{TiO}_2$  and  $\text{ZnO}$  are known to degrade certain organic sunscreens such as oxybenzone as well as antioxidants such as vitamins e.g. vitamins A, B, C and E. It will be appreciated that is particularly useful to use the doped  $\text{TiO}_2$  and/or  $\text{ZnO}$  with such sunscreens. This is because  $\text{TiO}_2$  and  $\text{ZnO}$  do generally have a positive UV absorptive effect. Thus by using the doped  $\text{TiO}_2$  and/or  $\text{ZnO}$  it may be possible to use less antioxidant or make the formulation longer lasting.

The organic solvents are typically from lower alcohols and polyols such as ethanol, isopropanol, propylene glycol, glycerin and sorbitol.

The fatty substances may consist of an oil or wax or mixture thereof, fatty acids, fatty acid esters, fatty alcohols, vaseline, paraffin, lanolin, hydrogenated lanolin or acetylated lanolin.

The oils are typically from animal, vegetable, mineral or synthetic oils and especially hydrogenated palm oil, hydrogenated castor oil, vaseline oil, paraffin oil, Purcellin oil, silicone oil and isoparaffin.

The waxes are typically animal, fossil, vegetable, mineral or synthetic waxes.

- 5 Such waxes include beeswax, Carnauba, Candelilla, sugar cane or Japan waxes, ozokerites, Montan wax, microcrystalline waxes, paraffins or silicone waxes and resins.

- 10 The fatty acid esters are, for example, isopropyl myristate, isopropyl adipate, isopropyl palmitate, octyl palmitate,  $C_{12}$ - $C_{15}$  fatty alcohol benzoates ("FINSOLV TN" from FINETEX), oxypropylenated myristic alcohol containing 3 moles of propylene oxide ("WITCONOL APM" from WITCO), capric and caprylic acid triglycerides ("MIGLYOL 812" from HULS).

- 15 The compositions may also contain thickeners such as cross-linked or non cross-linked acrylic acid polymers, and particularly polyacrylic acids which are cross-linked using a polyfunctional agent, such as the products sold under the name "CARBOPOL" by the company GOODRICH, cellulose, derivatives such as methylcellulose, hydroxymethylcellulose, hydroxypropyl methylcellulose, sodium salts of carboxymethyl cellulose, or mixtures of cetylstearyl alcohol and oxyethylenated cetylstearyl alcohol containing 33 moles of ethylene oxide.

- 20 When the compositions of the present invention are sunscreens they may be in the form of, for example, suspensions or dispersions in solvents or fatty substances or as emulsions such as creams or milks, in the form of ointments, gels, solid sticks or aerosol foams. The emulsions may further contain anionic, nonionic, cationic or amphoteric surface-active agents. They may also be provided in the form of vesicular  
25 dispersions of ionic or nonionic amphiphilic lipids prepared according to known processes.

The following Examples further illustrate the present invention.

The degradation of sunscreen formulation was assessed as follows:

## Methods:

### *Preparation of sample*

Cut two strips of polythene 10mm x 25mm and 12.5µm thick.

- 5 Lay the polythene strips 20mm apart on the centre of a quartz slide.

Pipette a drop of about 30µl of sunscreen preparation onto the centre of the slide.

Carefully lay a second quartz slide on top of the sample and squeeze the slides together at the polythene strips thus providing a specimen 12.5µm thick. Take care to avoid air bubbles.

10

### *Illumination*

Use a Xenon lamp filtered with a Schott WG320 filter to carry out illuminations.

Take a base reading of light output using a spectroradiometer calibrated between 290 and 400 nm.

- 15 Measure the light intensity (290-400nm) through a sample of water to use as a blank ( $I_q$ ). The intensity over the range 290 - 400 nm is typical of that found in moderate latitudes in mid-summer.

Measure the light intensity (290-400nm) through the sample ( $I_t$ ) at time 0 - as soon as it is put under the light - and then every 10 minutes for 1 hour.

- 20 At the end of the experiment take another base reading of light output to ensure that the light source has remained steady.

### *Calculations*

Calculate the transmission (K) of the sunscreen film at each individual wavelength:

25 
$$K = I_t / I_q$$

This can be used to plot wavelength vs transmission at each timepoint and shows the increase in transmission of an individual sunscreen during illumination.

- The loss of light absorption (D) by the sunscreen at each individual wavelength is  
30 calculated as the proportion of the absorption of the sunscreen at T=0 still remaining

at  $T=t$ :

$$D = K_0 / K_t$$

This can be used plot wavelength vs loss of light absorption. This plot allows comparisons to be made between different sunscreen preparations.

- 5 By measuring the area under this curve at each time point the rate of change of the total UVA absorption can also be calculated.

### *Formulations*

- 10 Commercial sunscreens Factor 5 and Factor 10. These have the following ingredients.

The ingredients in italics are the active sunscreen agents.

These formulations were modified by the incorporation of doped and undoped TiO<sub>2</sub> and ZnO in various concentrations and compared with unmodified formulations.

5

Commercial Factor 5

Aqua

C12-15 alkyl benzoate

10 Glycerin

Butylene glycol dicaprylate/caprate

Ceteareth-20

Glyceryl stearate

*Ethylhexyl triazone*

15 *Butyl methoxydibenzoylmethane*

*Disodium phenyl dibenzimidazole tetrasulfonate*

PVP/hexadecane copolymer

Tocophenylacetate

Cetyl palmitate

20 Cetearyl alcohol

Ceteareth-12

Phenoxyethanol

Methylparaben

Ethylhexylglycerin

25 Trisodium EDTA

Sodium citrate

Citric acid

PEG-4 laurate

PEG-4 dilaurate

30 PEG-4

Iodopropynyl butylcarbamate  
Perfume

Commercial Factor 10

5

Aqua

10 *Ethyl hexyl methoxy cinnamate*

Glycerin

Ceteareth-20

Butylene glycol dicaprylate/dicaprate

C12-15 alkyl benzoate

15 Glycerol stearate

*Ethylhexyl triazone*

*Butyl methoxydibenzoylmethane*

Phenoxyethanol

Cetyl palmitate

20 Cetearylalcohol

Ceteareth-12

PVP/hexadecane copolymer

*Phenyl/benzimidazole sulphonate*

Tocophenyl acetate

25 Methyl paraben

Ethylhexylglycerin

Trisodium EDTA

PEG-4 laurate

PEG-4 dilaurate

30 PEG-4



Iodopropynyl butylcarbamate

BHT

Perfume

5        The results are shown in the attached Figures in which:

Figure 1 shows the effect of time on absorption in UVA for a sunscreen formulation of factor 10 to which titanium dioxide, undoped or doped with 1% vanadium or manganese has been added.

Figure 2 gives the average percentage loss for several formulations.

10        Figure 3 shows the loss in absorption of a commercial factor 10 formulation in the UVA region at time = 0 up to t = 60.

Figure 4 shows the degradation of a factor 5 formulation to which has been added titanium dioxide doped or undoped.

15        Figure 5 shows the proportion of protection remaining for a commercial factor 10 formulation to which zinc oxide, undoped or doped with 1% manganese or iron has been added.

Figure 6 shows the average change in UVA absorption of a commercial factor 10 formulation to which has been added zinc oxide undoped or doped with manganese or iron.

20        Figure 7 shows the average change in UVA absorption for the same composition to which has been added  $\text{TiO}_2$  which has been coated or doped with manganese.

It can be seen that the addition of  $\text{TiO}_2$  and  $\text{ZnO}$  reduces the rate of degradation, this being due partly to scattering and partly to additional absorption.

25         $\text{TiO}_2$  or  $\text{ZnO}$  which is doped with manganese and vanadium, in particular, has a significantly greater effect in that the rate of loss of UV protection is reduced.

## CLAIMS

1. A cosmetic UV sunscreensing composition which comprises an amount of one or more organic components which are photosensitive and/or which  
5 are degraded by another ingredient of the composition, optionally together with an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has not been doped with a second element and an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has been doped with a second element, this composition having a rate of loss of UV absorption at least 5% less than that of a composition having the same formulation except that it does not contain the said  
10  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has been doped with a second element.
2. A composition according to claim 1 wherein the dopant is manganese, vanadium, chromium or iron.
3. A composition according to claim 2 wherein the dopant is  $\text{Mn}^{3+}$ .
4. A composition according to any one of the preceding claims wherein  
15 the dopant is present in an amount from 0.05% to 10 mole %.
5. A composition according to claim 4 wherein the dopant is present in an amount from 0.5 to 2 mole % by weight.
6. A composition according to any one of the preceding claims which comprises 0.5 to 20 mole % by weight of the doped  $\text{TiO}_2$  or  $\text{ZnO}$ .
- 20 7. A composition according to any one of the preceding claims wherein the doped material has a particle size from 1 to 200 nm.
8. A composition according to any one of the preceding claims which comprises doped titanium dioxide.
9. A composition according to any one of the preceding claims wherein  
25 the titanium dioxide is in rutile form.
10. A composition according to any one of the preceding claims wherein one or more of the said organic components is a UV sunscreen agent.
11. A composition according to claim 10 wherein the organic sunscreen agent absorbs UV light in the UVA region.
- 30 12. A composition according to claim 10 or 11 wherein the organic

sunscreen agent is a paraaminobenzoic acid, ester or derivative thereof, a methoxy cinnamate ester, a benzophenone, a dibenzylomethane, an alkyl- $\beta,\beta$ -phenyl acrylate, a triazine, a camphor derivative, an organic pigment, a silicone based sunscreen agent or 2-phenylbenzimidazol-5 sulphonic acid or phenyldibenzimidazol sulphonic acid.

5           13.    A composition according to any one of the preceding claims wherein the organic sunscreen agent is one which is degraded by  $\text{TiO}_2$  and/or  $\text{ZnO}$ .

          14.    A composition according to any one of the preceding claims which comprises 0.1% to 20% by weight of organic sunscreen agent(s).

          15.    A composition according to any one of the preceding claims which  
10 contains one or more of a fatty substance, organic solvent, silicone, thickener, demulsant, UVB sunscreen agent, antifoaming agent, moisturising agent, perfume preservative, surface activation filler, sequestrant, anionic, cationic, nonionic or amphoteric polymer, propellant, alkalising or acidifying agent, colorant or metal oxide pigment.

15           16.    A composition according to any one of the preceding claims which is a sunscreen.

          17.    A composition according to any one of the preceding claims which is in the form of a lotion, gel, dispersion, cream, milk, powder or solid stick.

          18.    A composition according to claim 1 substantially as hereinbefore  
20 described.

          19.    Use of a doped  $\text{TiO}_2/\text{ZnO}$  as defined in any one of claims 1 to 3 to reduce the concentration of one or more organic UV sunscreen agents or other ingredient which is photosensitive and/or is degraded by another ingredient in a cosmetic UV screening composition.

25           20.    Use of a doped  $\text{TiO}_2/\text{ZnO}$  as defined in any one of claims 1 to 3 to reduce the rate of loss in UV absorption of a sunscreen composition.

          21.    A method of increasing the effectiveness of an organic UV  
          sunscreening composition, which comprises one or more components which are  
          photosensitive and/or are degraded by another ingredient of the composition which  
30 comprises incorporating into the composition a doped  $\text{TiO}_2/\text{ZnO}$  as defined in any

-17-

one of claims 1 to 3.

# **ABSTRACT**

A cosmetic UV suncreening composition is described which comprises an amount of one or more organic components which are photosensitive and/or which  
5 are degraded by another ingredient of the composition, optionally together with an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has not been doped with a second element and an amount of  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has been doped with a second element, this composition having a rate of loss of UV absorption at least 5% less than that of a composition having the same formulation except that it does not contain the said  
10  $\text{TiO}_2$  and/or  $\text{ZnO}$  which has been doped with a second element.

Proportion of time 0 protection remaining after 60 minutes illumination

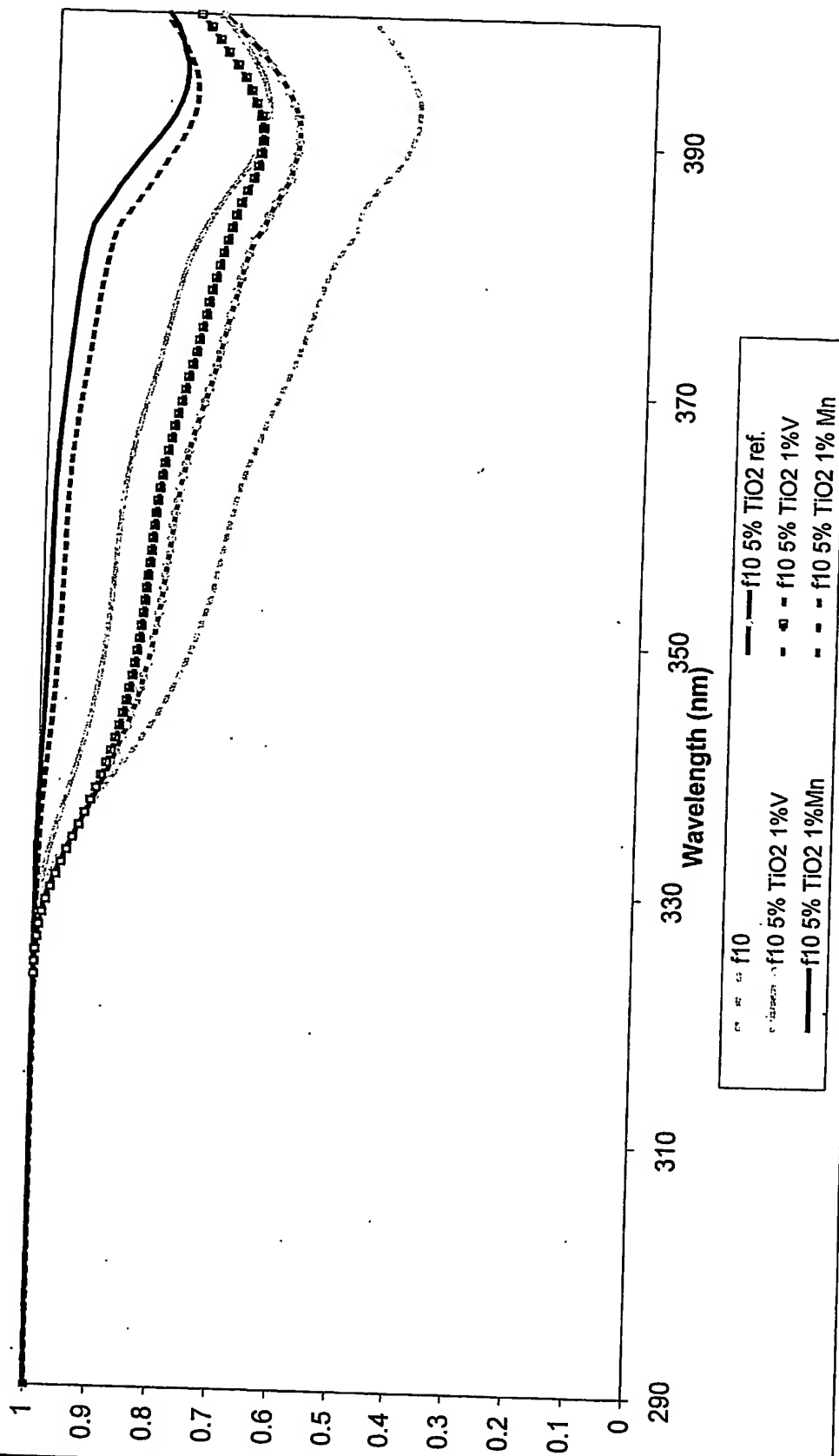


Fig.1

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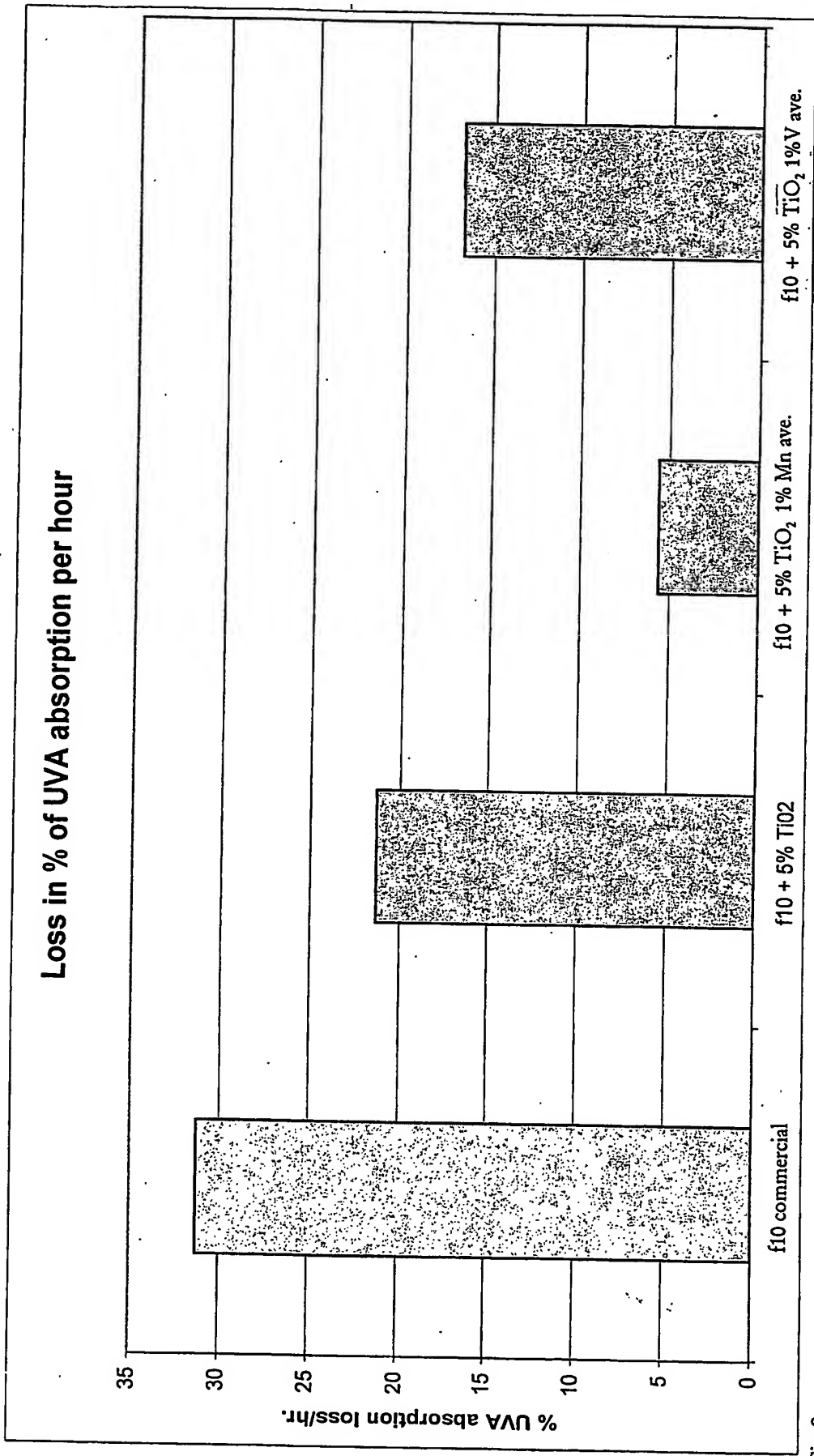


Fig. 2



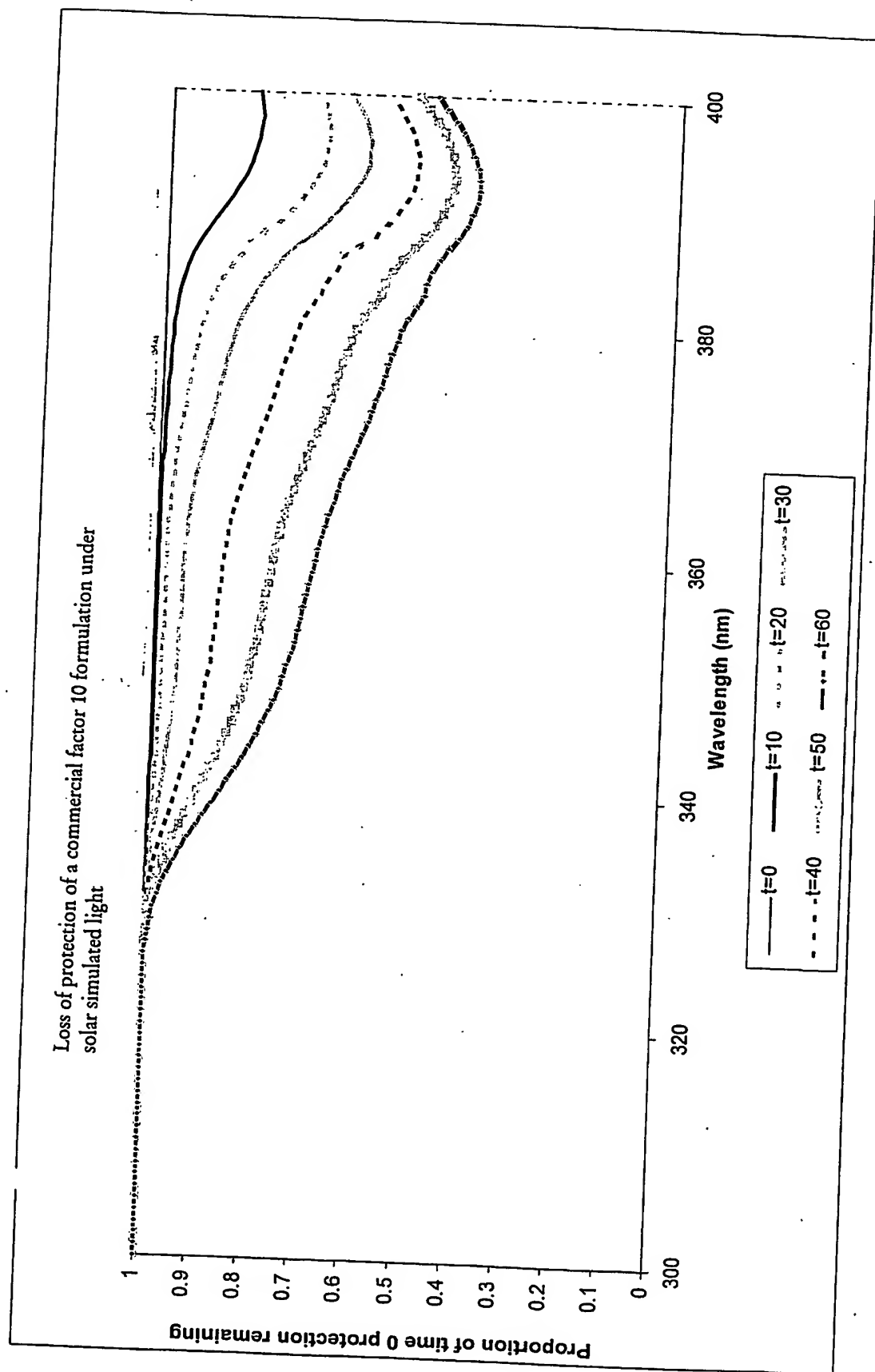


Fig.3

# factor 5 degradation with various TiO2

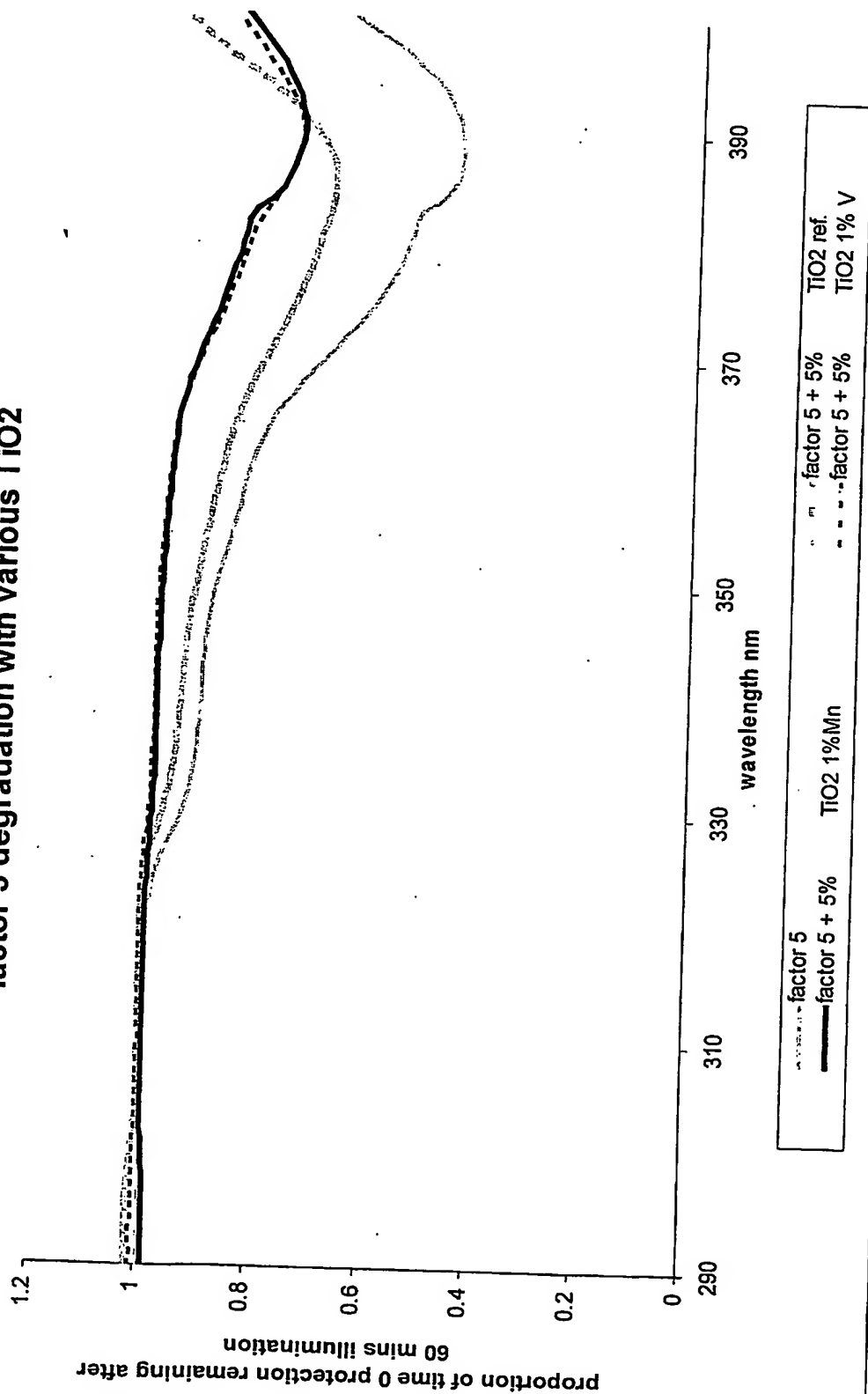


Figure 4

Proportion of time 0 protection remaining after 60 mins illumination

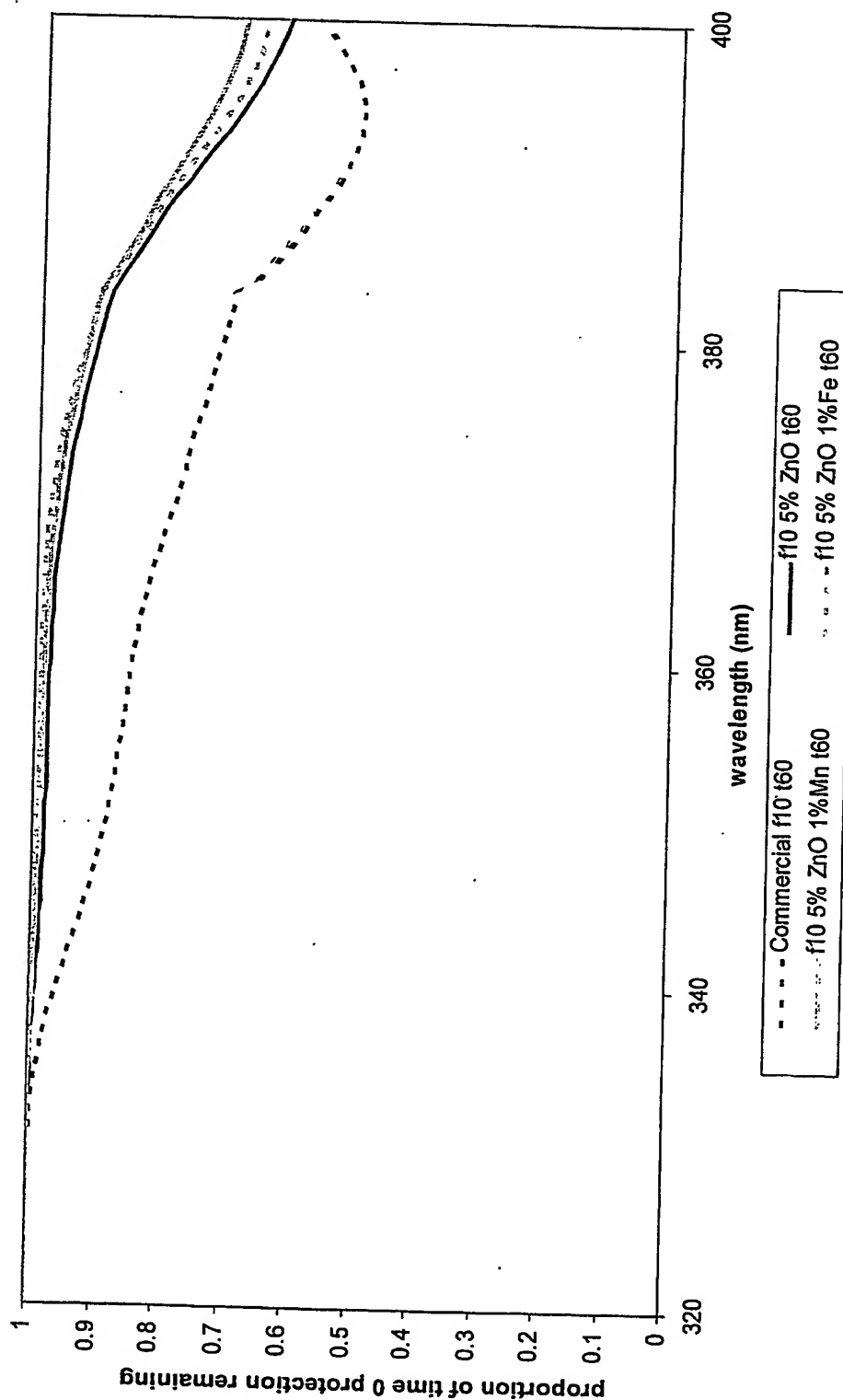


Fig 5

# Average change in UVA absorption per hour

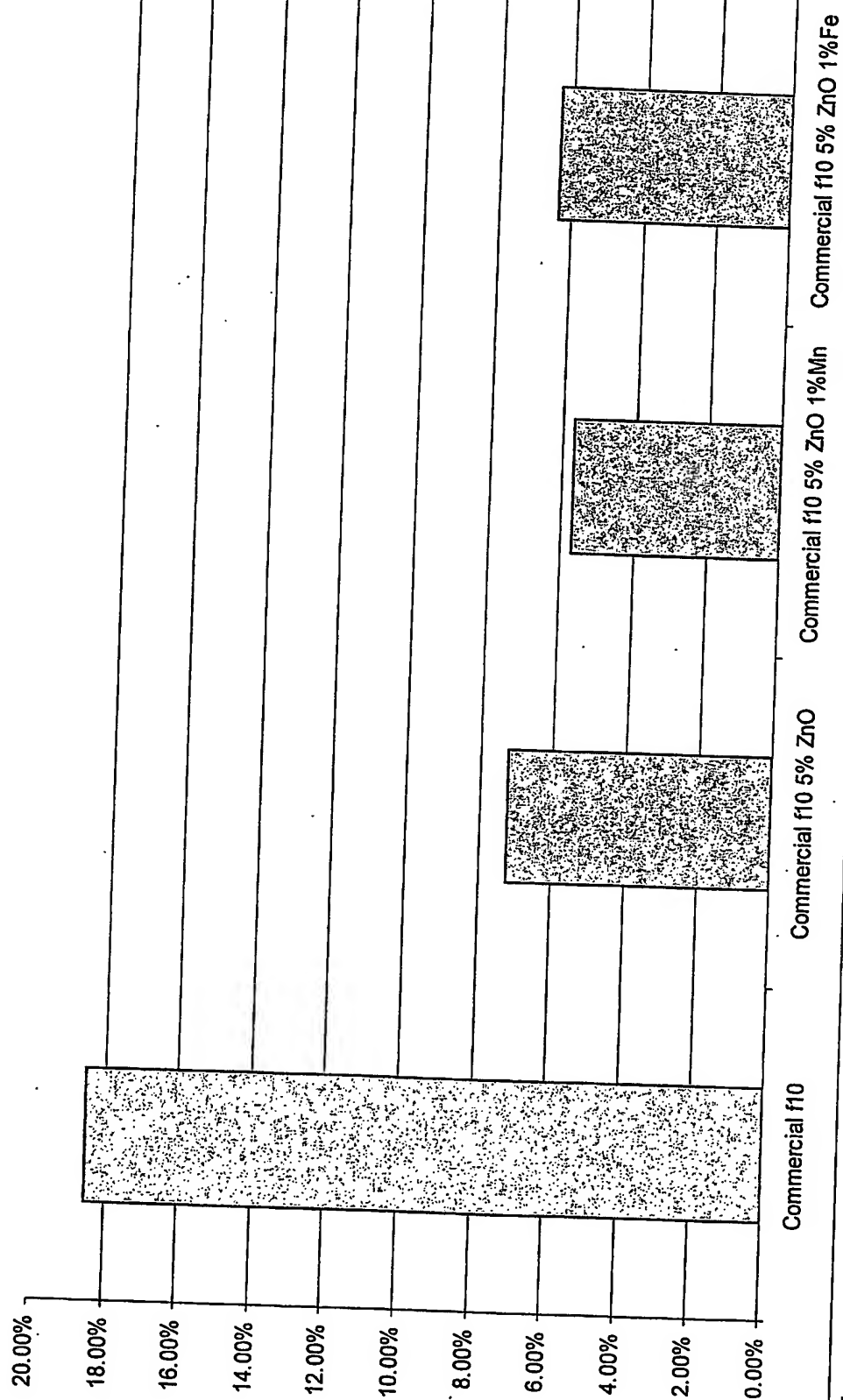


Fig.6

Average change in UVA absorption per hour

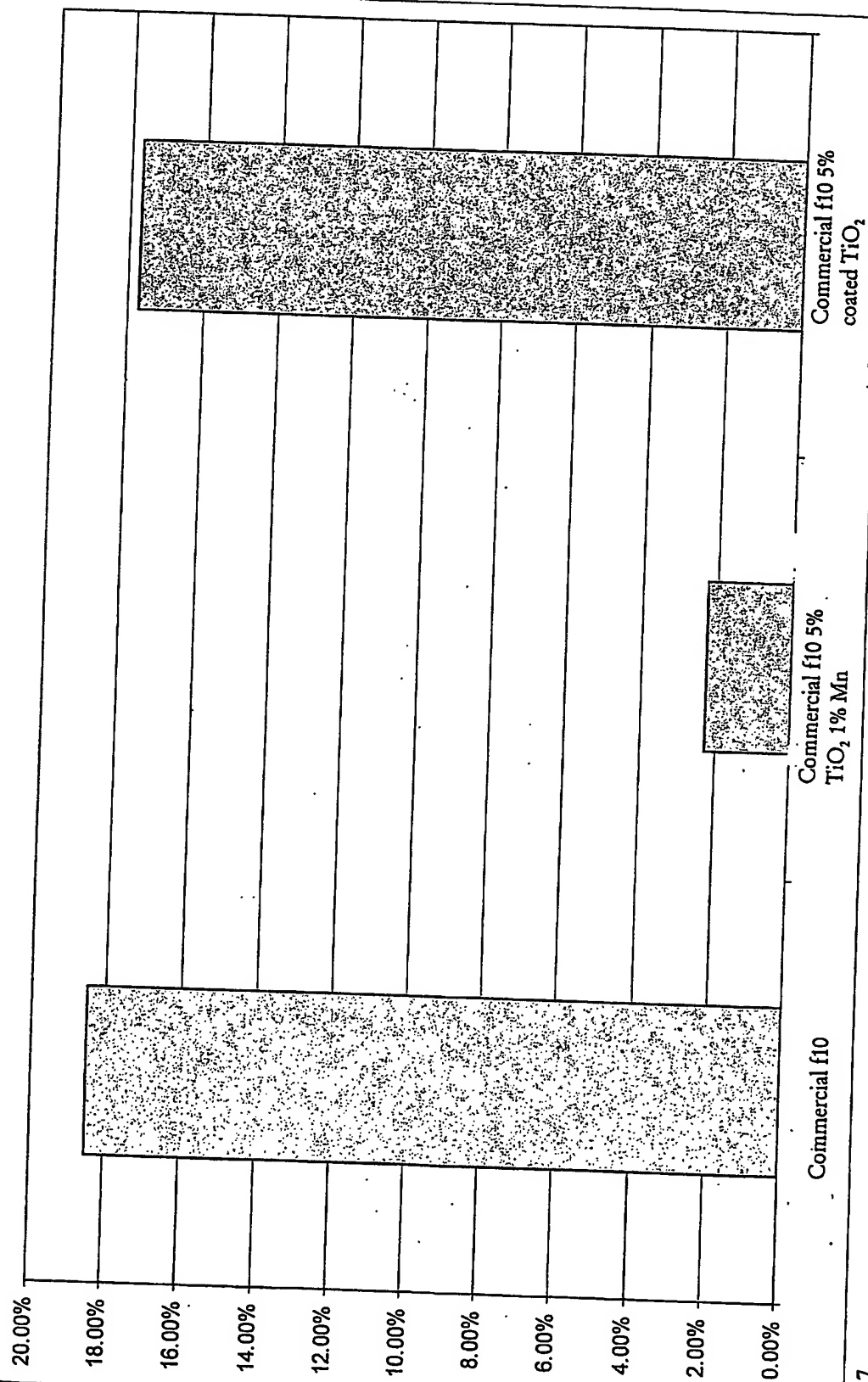


Fig. 7